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Harold H. Schobert

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Dr Julian Tishkoff

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14. ABSTRACT

Research was undertaken to develop coal-based jet fuel. The initial focus of the project was the development of a high heat sink fuel, JP-900, that could be used for thermal management, as well as for propulsion energy. In the most recent reporting period the focus shifted to development of a coal-based drop-in replacement for JP-8 fuel. Prototype fuel from hydrogenation of a mixture of light cycle oil and refined chemical oil met or exceeded all but four JP-8 specifications. The fuel had excellent low-temperature viscosity behavior and 0-ring seal swell comparable to JP-8. Deposition from thermal stressing of the fuel in various reactors was invariably lower than JP-8 or JP-8+100. Mechanisms of oxidative deposit formation for both jet and diesel fuels were proposed to account for the fact that the chemistry involved in both storage and thermal oxidative deposit formation in middle distillates was similar. The fuel was tested successfully in a T63 turboshaft engine, with emissions only slightly greater than JP-8.

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Submitted by

H. H. Schobert

Energy Institute
The Pennsylvania State University
University Park, PA 16802-2320

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ABSTRACT

This report summarizes briefly the key results of a project for the development of coal-based jet fuel. The initial focus of the project was the development of a high heat sink fuel, JP-900, that could be used for thermal management as well as for propulsion energy. In the last year the focus shifted to development of a coal-based drop-in replacement for JP-8. Prototype fuel from hydrogenation of a mixture of light cycle oil and refined chemical oil met or exceeded all but four JP-8 specifications. The fuel has excellent low-temperature viscosity behavior and O-ring seal swell comparable to JP-8. Deposition from thermal stressing of the fuel in various reactors was invariably lower than JP-8 or JP-8+100. Mechanisms of oxidative deposit formation for both jet and diesel fuels are proposed to account for the fact that the chemistry involved in both storage and thermal oxidative deposit formation in middle distillates is similar. The fuel was successfully tested in a T63 turboshaft engine, with emissions only slightly greater than JP-8. Well over a hundred publications resulted from the seven-year project period.

EXECUTIVE SUMMARY

This project originally focused on the development of an advanced, coal-based, thermally stable jet fuel, JP-900, which could serve for thermal management as well as propulsion energy. The project focus shifted in late 2005 to development of coal-based drop-in replacement for JP-8. Initial pilot-plant production was achieved by using a blend of refined chemical oil with light cycle oil, followed by hydrotreating and distillation. Tests by the Air Force Research Laboratory and University of Dayton Research Institute showed that the prototype fuel met or exceeded all but four JP-8 specifications. Two of the specification failures were simply because the prototype fuel was not additized prior to testing. The other two, low hydrogen and high density, could likely be corrected in a future pilot plant campaign. Furthermore, JP-900 had excellent low-temperature viscosity characteristics and O-ring seal swell behavior. The prototype fuel showed superb resistance to oxidative and thermal breakdown, producing solid carbon deposits in amount much less than JP-8 or JP-8+100. The fuel successfully operated in a T63 turboshaft engine. Although JP-900 showed increased engine emissions relative to JP-8, the magnitude of increase was much lower than other alternative fuels previously tested in this unit. The high density of JP-900 imposes a mass penalty on fuel consumption relative to JP-8.

In supporting laboratory work, solvent extraction processes have been developed to produce coal-derived feedstock, to eliminate the dependence on refined chemical oil. Refined chemical oil is a by-product of the metallurgical coke industry and is well known to be supply-constrained. A parallel route to JP-900, co-coking, has been shown to produce a by-product carbon that could have valuable uses in the aluminum anode, synthetic graphite, or activated carbon markets. A detailed mechanism of deposition was developed, which appears applicable for all middle distillate fuels and which combines oxidative and thermal degradation processes into a single mechanism. Combustion research in a high-pressure model gas turbine showed sooting propensity characteristics for JP-900 to be comparable to those of JP-8. Studies of combustion instability, carbon monoxide, and nitrogen oxides production also showed that JP-900 should be very similar to JP-8. Pulse detonation engines may be able to take advantages of the unique composition and density of JP-900.

During the period of performance over 120 papers were published on various aspects of this work. More remain to be written. Sixty graduate students received at least some support toward completion of the M.S. or Ph.D. degree. Many of these are now successfully pursuing energy- and fuel-related careers in industry or national laboratories.

99/07 FINAL REPORT

Introduction

Penn State University has been involved since 1989 in research on the development of jet fuel from coal. This work has been supported by the Air Force via a variety of mechanisms. The present report transmits key findings for work performed under Grant No. F49620-99-1-0290, which had a period of performance from July 1, 1999 through June 30, 2007. Supporting technical details are contained in over one hundred open publications (listed below) and the eight annual project reports already submitted.

From its inception until late 2005, this project focused on the development of a fuel of high thermal (i.e., pyrolytic) stability, which could be used both as the source of propulsion energy and as an on-board heat sink for thermal management. The target established by the Air Force was fuel that would be stable to 900°F for two hours. From the temperature requirement, the fuel was called JP-900. In meetings and conference calls held in late 2005 and early 2006, the Air Force requested that the emphasis of the Penn State work shift to development of a coal-based drop-in replacement for JP-8. Presumably, several factors motivated this shift, including (a) the Air Force's indication that there is no present need for a high-thermal-stability fuel for on-board thermal management; (b) collaborative work among the Air Force Research Laboratory, University of Dayton Research Institute, and Penn State showed that Penn State's prototype fuel met or exceeded most JP-8 specifications; and (c) the steady escalation in prices of crude oil and refined petroleum products resulted in increased interest in alternatives of potentially lower cost.

Description of Accomplishments

Project Overview

The overarching goal of the project has become the development of a cost-effective, coal-based, drop-in replacement for JP-8. To fulfill that goal, the project has been divided into three major technical focus areas: production of fuel, stabilization of the fuel, and its combustion behavior. Each of these areas is discussed very briefly in the subsections below.

Fuel Production

A substantial body of work done at Penn State in the early 1990s should clearly that an important key to meeting the thermal stability requirement of JP-900 was to have a fuel that was rich in cycloalkanes. Subsequently, additional benefits to this approach have become clear. First, although Fischer-Tropsch (FT) liquids appear to have great appeal in DOD alternative fuels planning, there is a very long time needed to build and commission such plants. The Sasol-II and –III complex in Secunda, South Africa took six years to build from the time the endeavor was given the go-ahead by the government. An unofficial estimate is that a similar-sized plant in the United States nowadays would require eight to ten years. The FT plant intended to be built in Gilberton, Pennsylvania has been in gestation for twelve years. Second, retrofitting existing refinery complexes to accommodate coal or coal liquids should substantially reduce the cost requirements, as well as time to come on stream.

Initially, three coal-to-refinery processes were considered: mixing coal-derived liquids from an off-site source with a suitable refinery stream, followed by hydrotreating the blend and distilling; adding coal to the feed being sent to a delayed coker, followed by hydrotreating the coker liquids and distilling; and "co-processing," the catalytic hydrogenation of a slurry of coal in a petroleum stream, such as a distillation residuum. The co-processing option was eliminated soon thereafter, because it is basically a "wrinkle" on direct liquefaction. The other two processes are being developed currently.

Coal-tar Blending

A vital aspect for meeting the high-temperature stability target of two hours at 900°F is a high concentration of hydroaromatic and cycloalkane compounds in the fuel. Cycloalkanes, e.g. decalin, possess a high degree of intrinsic thermal stability. In addition, they function as *in situ* hydrogen donors, stabilizing free radicals formed by bond cleavage during early stages of pyrolytic decomposition. Hydroaromatic compounds, e.g. tetralin, are good hydrogen donors, and also contribute to the shutting down of free radical reaction pathways that lead to fuel decomposition. In contrast, linear alkanes are especially prone to thermal decomposition at ≈900°F, and consequently are not desired components. Both cycloalkanes and hydroaromatics can in principle be made in high yields from coal by a variety of processes. Coals contain a variety of polycyclic aromatic structures, which, if liberated from the coal and hydrogenated, produce the desired cycloalkanes and hydroaromatics. (These considerations immediately eliminate coal gasification followed by Fischer-Tropsch synthesis, since gasification destroys the chemical "fingerprint" of the coal, and F-T synthesis produces abundant linear alkanes.)

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When this project was begun, the only coal-derived liquids available in commercial quantity were the coal tar fractions as by-products from metallurgical coke production. Of various possible coal-tar products, refined chemical oil (RCO) was found to be the best candidate [Butnark, 1999]. It was felt that this material would be a good surrogate for other coal-derived liquid products until such time as processing routes to make them could be developed. Laboratory-scale testing led to a standardized recipe of a 50:50 blend of RCO with light cycle oil (LCO), a by-product of catalytic cracking. Hydrotreatment of this blend, followed by fractionation, yields material boiling in the jet fuel range, meeting most JP-8 specifications, and possessing the high-temperature stability of JP-900. Distillation of the hydrotreated and hydrogenated product gives a product slate of about 6% gasoline, 80% jet fuel, 10% diesel, and 4% fuel oil.

A ten-drum batch of prototype JP-900 was produced in a pilot-plant campaign at Intertek-PARC, Harmarville, Pennsylvania. The hydrotreating and hydrogenation conditions for this campaign were selected, in part, in consultation with colleagues at United Refining Company in Warren, Pennsylvania to be able to operate in the hydrotreater equipment likely to be available in small refineries. The catalysts used are commercially available, so no new catalyst development is necessary.

Based on analyses conducted by the Air Force Research Laboratory, the properties of the prototype JP-900 are shown in Table 1. As evident from Table 1, prototype JP-900 meets or exceeds all but four of the JP-8 specifications. The high density of JP-900 also relates to its low hydrogen content. The high density derives in part from the high concentrations of cycloalkanes (Table 2) and correlates with hydrogen content. Likely, the hydrogen content could be brought within specification by slight adjustments in the hydrotreating and hydrogenation conditions in a future pilot-plant campaign. The other two specification failures arose simply because an additive package was not used in the prototype JP-900.

Low-temperature properties have been studied in detail, along with the effect of oxidation on these properties [Berkhous, 2007]. Particularly noteworthy are results in Figure 1 [Balster et al., 2007], showing excellent low-temperature viscosity behavior.

O-ring swell (Figure 2) [Balster et al., 2007] proved to be somewhat unexpected. This intriguing result on O-ring swelling has led to speculation about the validity of the conventional wisdom in this field. It has been argued that some concentration of aromatic compounds has to be tolerated in the fuel, despite their being precursors to soot, because the aromatics provide the seal-swelling capability. However, prototype JP-900 provides good swelling behavior despite its low concentration of aromatics, suggesting that it is not aromaticity of a compound (e.g., naphthalene) that provides the swelling behavior, but rather molecular shape (e.g., two-ring compounds such as both naphthalene and decalin).

Solvent Extraction of Coals

Despite the clear success of the coal-tar blending approach, available supplies of RCO are clearly limited, recognized in a detailed review published in 2002 [Schobert and Song, 2002].

Table 1. Prototype JP-900 composition, compared with maximum or minimum specification limits for JP-8.

ASTM Method	Test	Limits Min	Limits Max	JP-900 Lab Results
D3242	Total Acid Number (mg KOH/g)		0.015	0.000
D1319	Aromatics (%vol)		25.0	1.9
D3227	Mercaptan Sulfur (%mass)		0.002	0.000
D4294	Total Sulfur (%mass)		0.30	0.00
D86	Distillation			
	IBP (deg C)		Report	181
	10% Recovered (deg C)		205	192
	20% Recovered (deg C)		Report	194
	50% Recovered (deg C)		Report	204
	90% Recovered (deg C)		Report	243
	EP (deg C)		300	270
	Residue (%vol)		1.5	1.1
	Loss (%vol)		1.5	0.4
D93	Flash Point (deg C)	38		61
D5972	Freeze Point (deg C)		-47	-65
D445	Viscosity @ -20 deg C (cSt)		8.0	7.5
D3338	Heat of Combustion (BTU/lb)	18400		18401
D3343	Hydrogen Content (%mass)	13.4		13.2†
D1322	Smoke Point (mm)	19.0		22.0
D1840	Naphthalenes (%vol)		3.0	0.0
D130	Copper Strip Corrosion		1	1a
D3241	Thermal Stability @ 260 deg C			
	Tube Deposit Rating (visual)		<3	<1
	Change in Pressure (mmHg)		25	0
D381	Existent Gum (mg/100mL)		7.0	3.8
D5452	Particulate Matter (mg/L)		1.0	0.3
D1094	Water Reaction		1B	1b
D5006	FSII (DiEGME) (%vol)	0.10	0.15	0.00†
D2624	Conductivity (pS/m)	150	600	0†
D4052	API Gravity @ 60 deg F	37.0	51.0	31.1†

† Lab results out of specification limits.

The essential limitation of RCO supplies was reaffirmed in a study conducted by the RAND Corporation [Bartis and Flint, 2007].

As recognized following the 2002 review, it is vital to develop a "neo-RCO" that retains the same chemical features as the original RCO, and that could in principle be produced in slightly retrofitted refinery capacity. Of course, low production cost is also very desirable. Presently such development work focuses on solvent extraction of coal.

Since the goal is eventually to blend the coal-derived extract with LCO, it seems easiest to use LCO itself as the extracting solvent. If it were possible to obtain a high-enough

Table 2. Compound classes present in prototype JP-900 fuel.

Summarized D2425	Volume %
Paraffins	<1.0
Cycloparaffins Sum of mono, di- and tri- cycloparaffins	97.3
Alkylbenzenes	<1.0
Indan and Tetralins	1.6
Naphthalene/naphthalenes	<1.0
HPLC - D6379	Volume %
Monoaromatics	2.1
Diaromatics	< 0.1
Total Aromatics	2.1
Saturates (by difference)	97.9

concentration of coal extract in the LCO, the extract-LCO stream could go directly to hydrotreating without need for solvent stripping and solvent recycle operations.

Current work shows that best yields were obtained with Pittsburgh, Illinois, and Blind Canyon (Utah) bituminous coals. With a 10:1 ratio of LCO and coal at 350 °C in a laboratory-scale multistage reactor, the yield from Pittsburgh coal was ≈73% in the third stage. A present focus is on reducing the amount of solvent needed, with the goal of making a 1:1 LCO/coal liquid for further hydrotreatment, and reducing the extraction temperature. Future work will investigate other prospective solvents and possible uses for the extraction residue.

A collaboration has been established between the Penn State group and colleagues in the Separation Science and Technology focus area, North-West University, Potchefstroom,
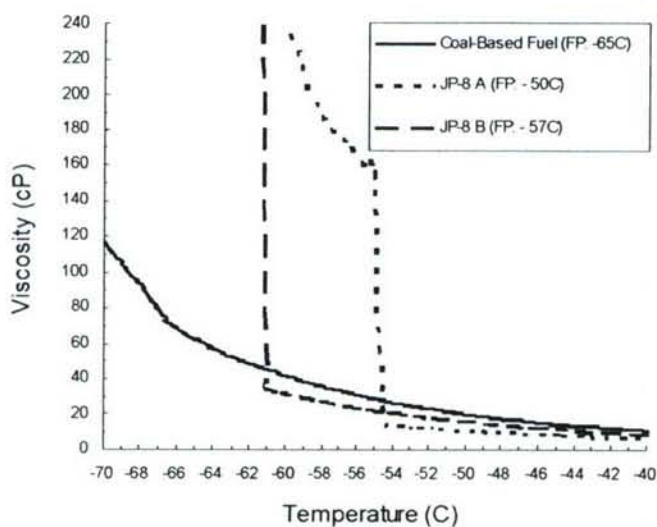

Figure 1. Viscosity behavior of prototype JP-900 compared with two samples of JP-8.
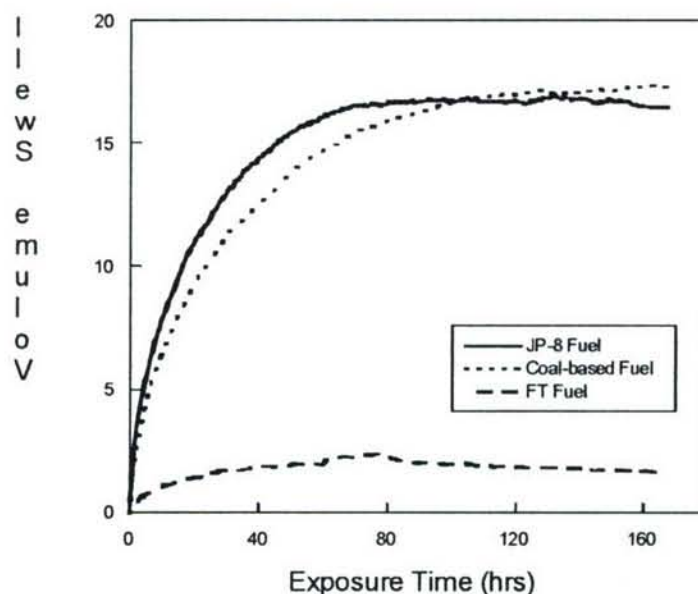
Figure 2. O-ring swelling of prototype JP-900, compared with JP-8 and a Fischer-Tropsch jet fuel.

South Africa. The principal joint activity is in designing, constructing, and operating a system for multi-stage continuous extraction. No AFOSR funds have been expended on this collaboration, but it is mentioned here because of its direct bearing on this project and on the concerns raised by RAND. The South African contribution is largely funded by Sasol.

Co-coking

Co-coking was selected for investigation as an alternative means of introducing coal into oil refinery operations for the production of JP-900. It is also an approach to development of coal-based jet fuel that does not link fuel production to products from a metallurgical coke plant. The concept is that coal would be blended into the feed stream to a delayed coker. The coker liquids, which would be expected to contain some of the light pyrolysis products from the coal, would then be hydrotreated, hydrogenated, and fractionated to produce the desired jet fuel. The sale of the "co-coke" could produce a by-product revenue stream that would help offset the processing costs for the liquid fuel, especially if the coke could be shown to be a premium product having value in excess of that for a simple fuel coke.

Initial scouting studies considered atmospheric distillation residua and decant oil as prospective petroleum components, and highly fluid bituminous coals as the likely coal feed. Continued work selected decant oil as the desirable petroleum feed, since decant oil is the precursor to highly valuable needle coke. Future work will include resids and other possible refinery-stream feedstocks.

In microautoclave tests, of the coker liquids showed that coal-derived aromatic components were contributing to the <300°C boiling fraction, and that polar compounds from

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the coal, such as phenols, were ≤0.4% [Escallón, 2004]. In addition, the coke appeared to be highly graphitizable, as will be discussed below.

On the basis of these encouraging preliminary findings, a larger-scale coker was constructed, copied from an existing unit at Intertek-PARC, so that data from the Penn State unit could eventually used for scale-up to even larger pilot-scale cokers at PARC. Using 4:1 decant oil to ultra-clean Pittsburgh seam coal at ~465°C and 25 psig, the products are 27% coke, 10% gas, and 63% liquid. The liquids were: about 2% gasoline, 5% jet, 5% diesel, and 86% fuel oil/pitch. It is important to note that these liquids were not hydrotreated. We expect that any hydrocracking accompanying hydrotreatment downstream of the coker will shift the product distribution to enhance the yield of lighter fractions. The jet fuel fraction of the non-hydrotreated liquid consists mainly of alkanes and two-ring compounds. The fuel oil fraction will contain the heaviest components, and has been fractionated to produce pitch. Production of a good-quality binder pitch could represent another high-value premium by-product from this process, since there is a world-wide shortage of coal tar pitch.

Ideally the by-product coke must be a material that has a higher market value than fuel coke (also known as shot coke). To be compatible with large commercial-scale fuel production, this market needs to be for a product that has high-tonnage applications. The potential applications for coke that are both high-value and high-tonnage are: a filler for the production of aluminum-smelting anodes, a filler for the production of synthetic graphites, a starting material for production of activated carbon, a reductant in metallurgical processes (e.g., a replacement for blast-furnace coke), and as carbon black. Encouraging preliminary data have been obtained on the first three of these applications.

Collaborative work with Alcoa showed that coke from ultra-clean coal was of good quality for aluminum-smelting anodes, though the iron and silicon in the carbon did not meet specifications [Badger et al., 2002]. These preliminary results are highly encouraging, but reducing levels of inorganic contaminants below specification limits is a thorny problem. We are considering further coal-cleaning strategies and characterizing the coke in more detail to determine other uses. Another approach has been to extract coal with decant oil in order to feed an ashless material the coker to meet mineral specifications for anodes and electrodes. This is in progress under the newly established contract with AFOSR; results will be presented in future annual and final reports.

One alternative high-value, high-tonnage application for coke is as the filler in the production of extruded graphite electrodes, or molded graphites for specialty applications, e.g., electrical discharge machining. Commercial graphites are made by mixing a filler (currently needle coke from delayed cokers) with a binder, usually coal tar pitch, baking, and graphitizing. Success depends on having a filler that is itself graphitizable. That is, the graphitizing ability of the filler—in this case, the coke from co-coking—is key. Initial work used a graphitization temperature of 2280°C. X-ray diffraction results are shown in Table 3 [Escallón, 2004]. For graphitization, 2280°C is a low temperature. Increasing graphitization temperature to 2900°C reduced the interlayer spacing to 3.356 Å, which compares quite well with the value for graphite, 3.354 Å. These results suggest that the coke from co-coking could have value as a feedstock for graphite production.

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Table 3. Comparison of principal X-ray characteristics of coke from co-coking with needle coke, for graphitization at 2280°C.

	Interlayer spacing, Å	Stacking height, Å	Degree of graphitization
Coal-petroleum co-coke	3.360	382	0.93
Commercial needle coke	3.370	250	0.81

Another alternative is use of "co-coke" for activated carbon production. Cokes were activated by reaction with potassium hydroxide at 700°C for 60 minutes under flowing nitrogen. Activated cokes from two different bituminous coals reacted with decant oil (25% coal in decant oil) had surface areas of 1720 and 1840 m^2/g. Most of the surface area of both activated cokes is in the micropore region, making them particularly useful in gas-phase applications for, e.g., environmental systems.

Fuel Stability

Stability of Prototype JP-900

The initial challenge established by the Air Force was for the development of a fuel that would be stable to 900°F for two hours. We have successfully met this challenge.

Colleagues at the Air Force Research Laboratory and the University of Dayton Research Institute used a quartz-crystal microbalance (QCM) to study the stability of JP-900 [Balster et al., 2007]. QCM has been used in other studies at these organizations to examine fuel stability and to qualify various jet fuel additives. QCM monitors both headspace oxygen concentration and carbon deposition in situ during stressing. The QCM is a batch test normally operated at 140°C for 15 hours using air-saturated fuel samples. In the QCM, JP-900 consumed all of the available oxygen very rapidly compared with JP-8. This behavior is exhibited by solvents, such as Exxsol D110 (an aliphatic hydrocarbon blend), and by heavily hydrotreated fuels that do not contain antioxidants [Zabarnick, 1998]. In contrast, JP-8 consumed oxygen more slowly, reducing the headspace oxygen by only 65%, and producing a slowly oxidizing profile typical of a fuel with antioxidant (e.g., alkylphenols) present. Only 0.3 $\mu g/cm^2$ of surface deposit was produced by stressing JP-900. This deposit is substantially lower than from JP-8 samples, which ranges from ≈2 to 8 $\mu g/cm^2$. For further context for these deposit values, a maximum passing value of 1.0 $\mu g/cm^2$ was established for the evaluation of JP-8+100 additive candidates [Balster et al., 2007]. The relatively low amount of deposit produced by JP-900 can be attributed to the lack of heteroatomic species such as phenols, sulfides, and nitrogen compounds.

The ECAT flow reactor system at the Air Force Research Laboratory was used to evaluate the oxidative stability of JP-900 under complete oxygen consumption conditions [Balster et al., 2007]. The experiments in this study were conducted using a 50-inch long, 0.125-inch o.d., 0.085-inch i.d. tube constructed of 316 stainless steel, a reaction pressure of 550 psig and a volumetric flow rate of 10 mL/min. The furnace temperature was set to obtain a
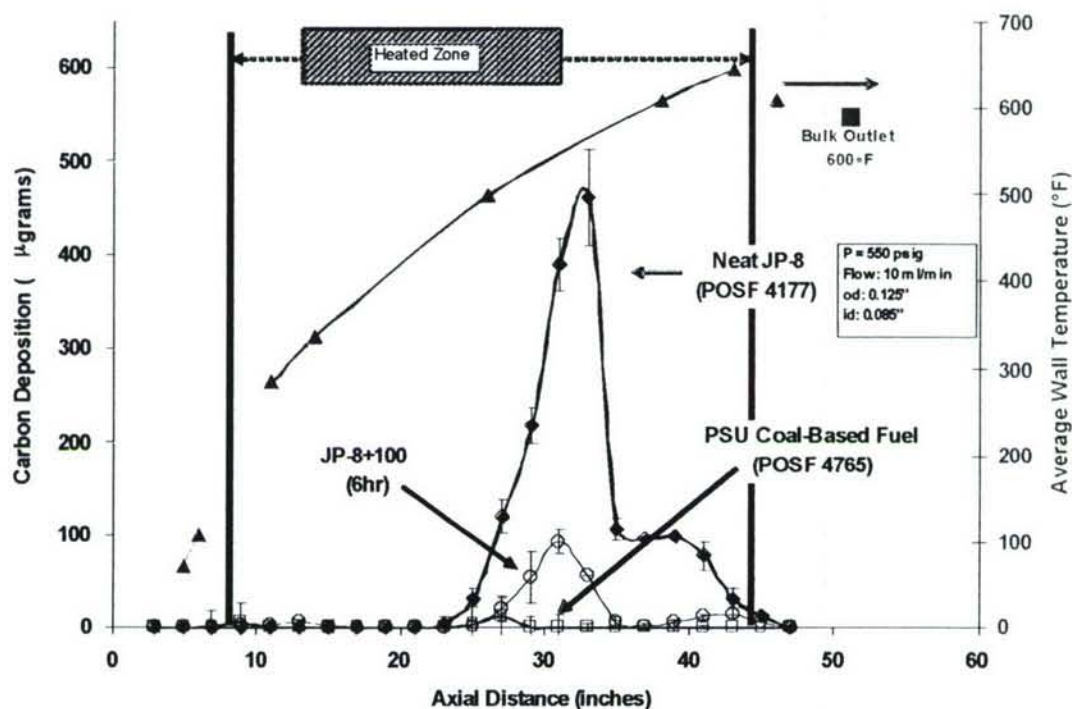
Figure 3. Surface deposition of prototype JP-900 fuel compared with JP-8 and JP-8+100.

target maximum wall temperature of 650°F (bulk ≈600°F), which provided a total residence time of ≈20 seconds in the actively heated zone for the specified reaction conditions. These reaction conditions have previously been shown to provide complete consumption of the dissolved oxygen in the fuel within the reaction zone. Studies were conducted to compare the oxidative stability characteristics of JP-900 with a typical JP-8. Testing was conducted with a total reaction time of eight hours. A comparison of the surface deposition profiles for the 8-hour testing with JP-900 and JP-8 is shown in Figure 3 [Balster et al., 2007].

JP-900 demonstrated excellent oxidative stability, producing minimal deposition on the reaction tube. Bulk deposits collected on the downstream filter were reduced by an order of magnitude (approximately 270 µg versus 2660 µg for JP-8). The improved stability of JP-900 is most likely due to the absence of heteroatom-containing species that have been implicated as promoters of deposit formation. The stability of JP-900 is similar to JP-7, a specialty fuel designed to be stable for high-temperature applications. JP-900 demonstrated excellent stability under a complete oxygen consumption regime. The stability was better than that obtainable for a JP-8 fuel with the use of the currently qualified JP-8+100 thermal stability additive package. The surface deposition for the JP-8 dosed with the specified treat rate of the JP-8+100 for a reaction time of six hours is also shown in Figure 3. Although deposition using the JP-8+100 additive package is significantly reduced relative to JP-8, it is much higher than for JP-900. This further demonstrates the improved oxidative stability characteristics of JP-900 relative to JP-8.

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Mechanistic Studies

The processes involved in the formation of thermal oxidative deposits in aviation turbine fuels were summarized by Hazlett [Hazlett, 1991]. There is an inverse relationship between the temperature at which a fuel absorbs oxygen and the amount of thermal oxidative deposit. Fuels that absorb dissolved oxygen at lower temperatures, such as highly hydrotreated fuels, tend to form smaller amounts of deposit. Fuels that absorb dissolved oxygen at higher temperatures tend to form larger amounts of deposit. This inverse relationship is consistent with a peroxyl radical chain mechanism. Oxidation is focused on the fuel's indigenous antioxidants (i.e. phenols, arylamines, and thiols). Since such molecules contain weak O-H, N-H, and S-H bonds, they are prone to hydrogen atom abstraction by peroxyl radicals. The oxidized indigenous antioxidants then react with molecular oxygen and ultimately form oxidative deposit within the engine. Similar chemistry is involved in deposit formation for both storage and thermal oxidative degradation of middle distillates in general [Beaver et al., 2005].

We propose that the mechanisms of oxidative deposit formation for both jet and diesel fuels are mechanistically similar. In addition, we propose that the chemistry involved in both storage and thermal oxidative deposit formation in middle distillates is similar. Making such connections is complicated by the fact that most studies on diesel oxidative stability involve ambient storage stability issues while jet fuel research is usually focused upon thermal stability. A fundamental understanding of the chemistry involved is further complicated by the fact that different fuels, derived from both different crudes and processing conditions, will exhibit different stabilities.

We propose the mechanism in Scheme A (Figure 4) to account for the formation of thermal oxidative deposits in jet fuels. It must be stressed that the proposed mechanism is generic in that the illustrative molecules merely are representing general classes of chemical reactions. It is important to note that these general classes of reactivity, generically described as autoxidation followed by coupling reactions, are not new. Recent results have enabled a better mechanistic understanding of some of the details for oxidative deposit formation.

In Scheme A (Figure 4), jet fuel degradation begins with oxidation, by peroxyl radicals, of indigenous antioxidants such as phenol (1). The resultant phenoxyl radical can react with molecular oxygen. The resultant keto peroxyl radical (2), upon dimerization, yields tetraperoxide (3). Decomposition of (3) yields molecular oxygen in addition to hydroquinone (4) and quinone (5). Both organic products are only marginally fuel-soluble but are subsequently captured by reactions leading to formation of more soluble species. Hydroquinone (4) is more reactive, both oxidatively and nucleophilically, than the phenol from which it is derived. Quinone (5) is a potent electrophile and can be thought of as a 'coupling catalyst' for fuel deposit formation. To illustrate this, step 5 shows an electrophilic aromatic substitution (EAS) reaction of quinone (5) with an electron-rich heterocyle, a substituted carbazole, to form a new coupled molecule. The product of step 5 has a molecular formula of $C_{21}H_{19}O_2N$.

As shown in Scheme A (Figure 4), further oxidation of compound (6) to a quinone (7), followed by subsequent electrophilic aromatic substitution with hydroquinone (6) yields compound (8). This compound has a molecular formula of $C_{21}H_{18}O_2N$ and a mass of 632.
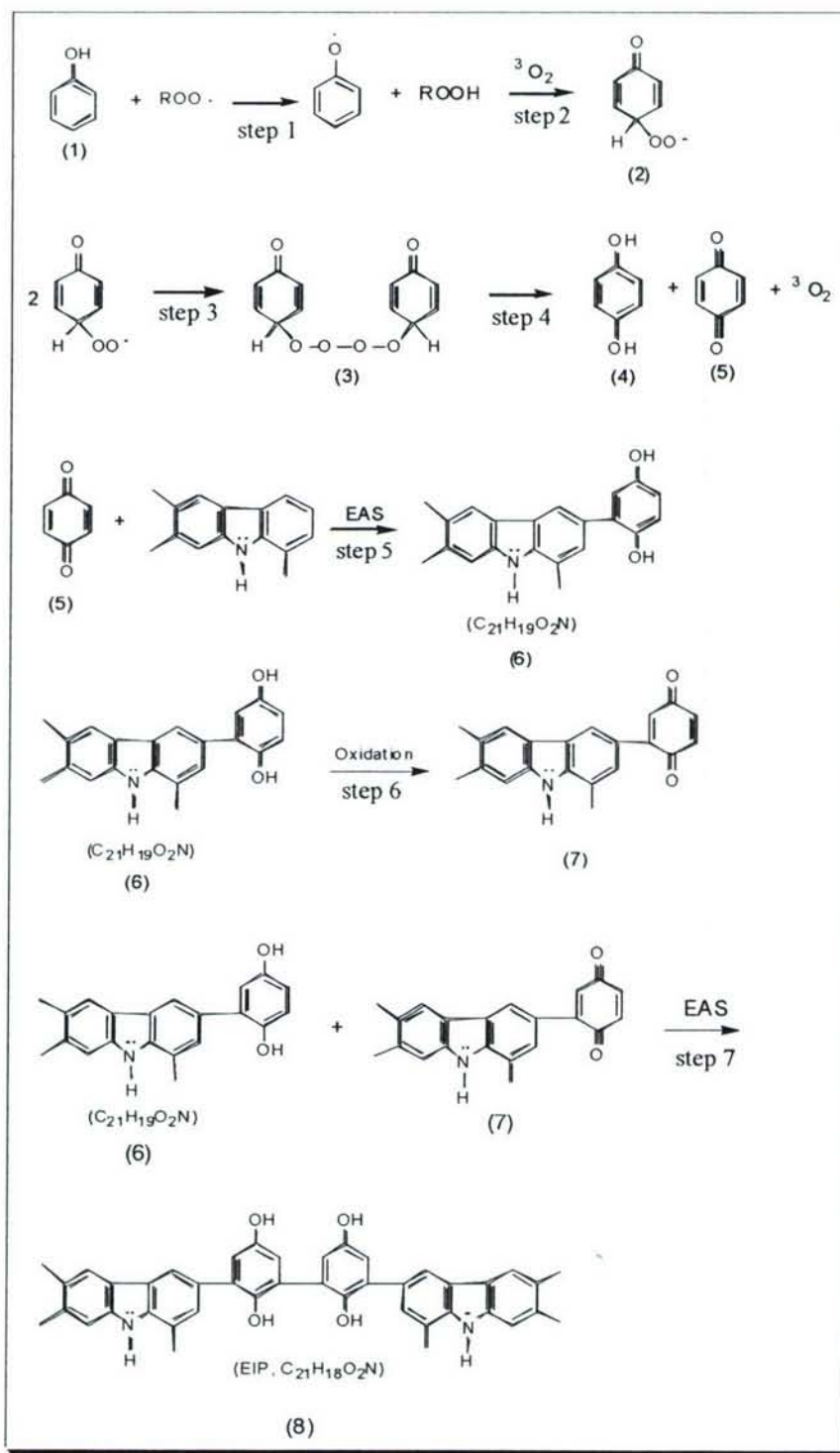
Figure 4. Scheme A for thermal oxidative deposit formation in jet fuels.

Rapid precursor oxidation is due to the enhanced reactivity inherent in the molecular structure generically represented in the scheme as compound 8.

As conceptualized in Scheme A (Figure 4), jet fuel oxidative deposit formation occurs after compound (8) is coupled to another large molecule. The mechanistic details could involve oxidation of (8) to the corresponding quinone (not shown); thermally promoted EAS with a reactive electron-rich substrate, such as unreacted compound (8), to yield a larger molecule. The resulting coupling product would have a mass greater than 1200 and would be expected to be insoluble in the fuel. Agglomeration of bulk fuel insolubles would yield microspherical particles, which then precipitate.

In Figure 5 are results for stressing JP-8 to a fuel temperature of 625°C in a flowing rig with a Silcosteel surface, both in the presence and absence of air. These results suggest that oxidative deposit formation occurs at temperatures well above the temperatures that previous work has found for complete oxygen consumption with Silcosteel, ~225°C bulk fuel temperature (i.e. 15 cm in Fig. 5) or ~ 325°C wall temperature.

The proposed mechanism, or a slight variation of, can explain three recently reported experimental observations for fuels stressed at high temperatures in flowing rigs at temperatures with complete oxygen consumption (350°C). These observations are: a limited dispersant effect upon deposit formation with a stainless steel surface; a minimization and delay of oxidative deposit formation with a Silcosteel surface; and additivity in oxidative deposit minimization with use of both a Silcosteel surface and dispersant.

In Scheme A (Figure 4), formation of bulk fuel deposits can be minimized with a dispersant by limiting insolubles agglomeration. However, once this pathway has been minimized, additional dispersant does not affect deposition. Presumably, a second deposit
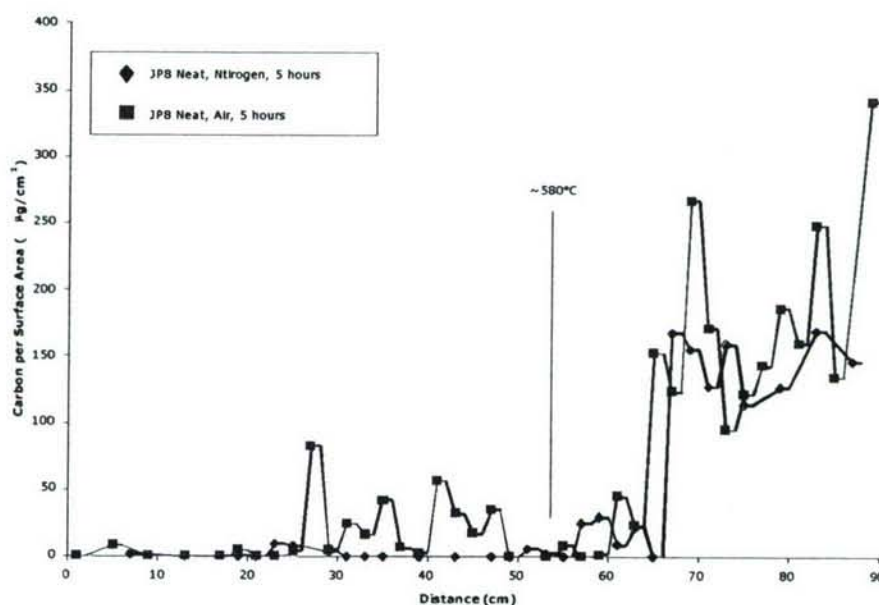

Figure 5. Carbon deposition profile- JP8 neat, 625 C, 5 h, air vs. nitrogen (550 psi).

pathway exists which is not affected by dispersant. We suggest the mechanism proposed in Scheme B (Figure 6) as a stainless-steel surface-promoted deposit pathway. Reaction starts with the interaction of the fuel's indigenous aryl thiols with reactive sites on stainless steel as shown in step 1. The mechanistic details of this step are unknown. However, it is proposed that a metal sulfide is generated at the stainless steel surface. Such a species is proposed, due to electronic donation of the sulfide to the aromatic ring, to be highly activated towards electrophilic aromatic substitution. As shown in steps 2 and 3, reaction of the metal sulfide with electrophiles, formed in Scheme A (Figure 4), would yield an incipient surface deposit. Owing to the enhanced reactivity of the aromatic metal sulfide towards electrophilic aromatic substitution, a dispersant would not slow this reaction rate significantly.

The metal-bound aryl sulfide shown in Scheme B (Figure 6) is proposed to be a reactive nucleophile which can couple with electrophilic sites. Since agglomeration is not a part of the deposit forming mechanism, dispersants would not affect these reactions. However, surface passivation with Silcosteel will inhibit these surface reactions.

The formation of oxidative deposit at high temperatures with Silcosteel is consistent with the hypothesis articulated in Scheme A (Figure 4). The proposed mechanism can account for the observed dispersion of oxidative deposit over a wide range of temperatures (with different fuels) well beyond the temperature of complete oxygen consumption. In addition, the new level of
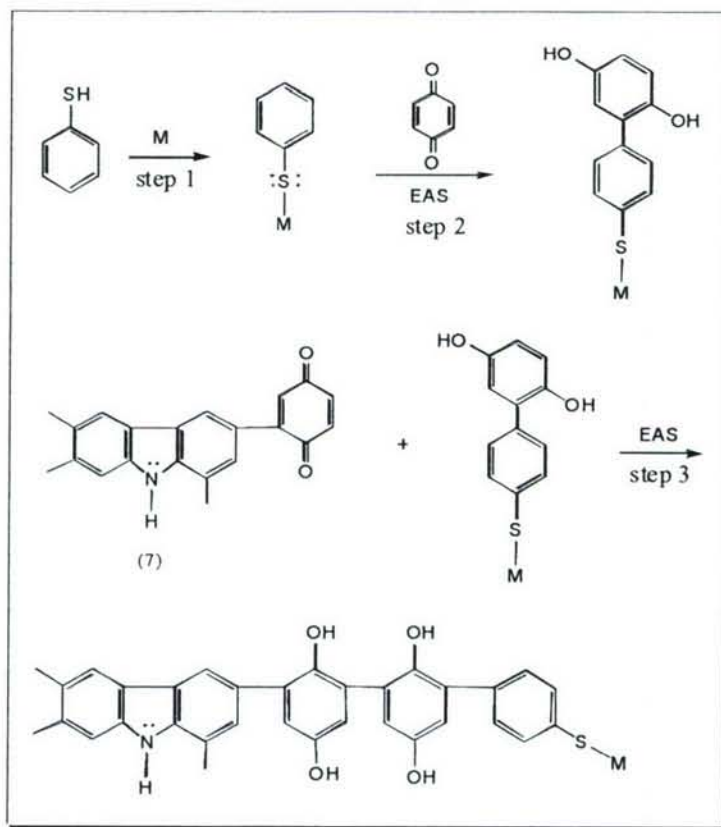

Figure 6. Scheme B, a stainless-steel-surface promoted pathway to deposition.

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mechanistic understanding will provide new insights into the chemistry of deposit formation for middle distillate fuels in general. Any hydrogen-containing heteroatomic aromatic species, such as phenols, aryl amines and thiophenols, can be oxidized to electrophilic quinone species. These same molecules in their non-oxidized form, in addition to other aromatic electron-rich heteroatom-containing compounds, can be nucleophilic species. The order of decreasing nucleophilic reactivity is proposed to be: indoles and carbazoles > benzofurans > benzothiophenes. Oxidative deposit ultimately results from coupling electrophilic and nucleophilic species by EAS reactions.

The fundamental chemistry involved in oxidative deposit formation under both storage and thermal conditions is similar. It is also suggested that the presence of copper in a fuel will catalytically promote deposit formation by accelerating peroxyl chain chemistry, by chain branching. Reaction of peroxyl radicals with the fuel's indigenous antioxidants initiates both storage and thermal oxidative instability.

Future engine technologies will increasingly stress fuels to higher temperatures prior to combustion for both performance and environmental reasons. The proposed mechanism for middle distillate oxidative degradation suggests focusing stabilization efforts upon minimizing reactive electrophilic quinone formation should be fruitful. Silylation of the fuel's indigenous antioxidants would block electrophilic quinone formation and presumably limit oxidative deposit formation. In addition, development of oxygen-scavenger additives to limit fuel quinone formation should also be effective.

Fuel Combustion

High-pressure Model Gas Turbine Studies

Combustion studies were conducted to investigate performance and emissions characteristics of JP-900. Experimental operating conditions were selected to address the actual operating conditions of a gas turbine jet engine combustor. This required experiments to be conducted at high pressure and with preheated air. The requirement for pre-heated air is to simulate the outlet conditions of the jet engine compressor, which produces high-pressure air at an elevated temperature that is a function of the operating compression ratio of the compressor.

High-pressure combustion studies of the atomization and combustion instability characteristics for early production runs of coal-based JP-900 indicated that the breakup and atomization processes for these fuels were essentially equivalent or slightly superior to JP-8. Comparison of the pollutant emissions from the combustion of coal-based JP-900 and JP-8, specifically in terms of oxides of nitrogen and carbon monoxide, were also quite similar. The major emission product that significantly exceeded that observed for JP-8 was soot particle emission. Thus, recent combustion studies of subsequent production of coal-based JP-900 have focused on the soot emission measurements.

The model combustor was operated at a pressure of 0.51 MPa having an air inlet temperature of 550 K with an air flow rate of 32 g/s. The fuel flow rate was varied to achieve a range of equivalence ratios between 1.0 and 1.5. These fuel-rich equivalence ratios were
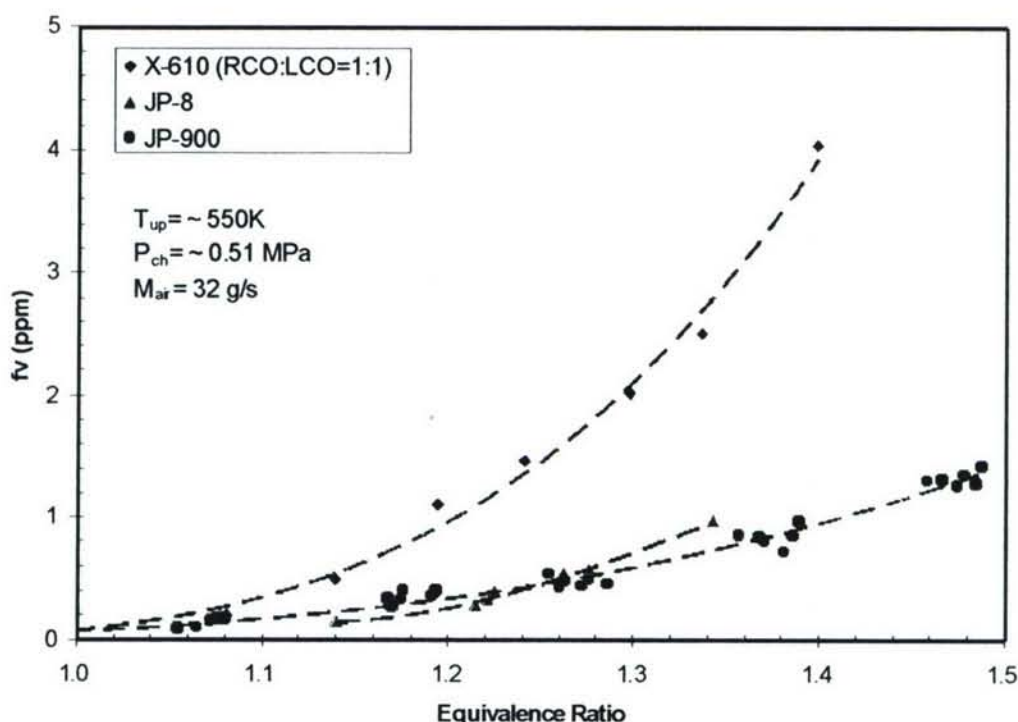
Figure 7. Soot volume fraction in ppm as a function of equivalent ratio for JP-900, JP-8 and coal based fuel X-610.

selected to provide sufficient quantities of soot particles for accurate measurements of the soot volume fraction that would result in meaningful comparison of the relative soot formation characteristics of the prototype JP-900 with respect to conventional JP-8. Both the prototype JP-900 and the conventional JP-8 studies were conducted under identical operating conditions and measurement procedures. Measurements obtained for the two fuels were identical in terms of their soot formation characteristics within the measurement accuracy of the laser extinction technique. Results of these studies of the prototype JP-900 and JP-8 are shown in Figure 7. The results for an earlier production run for the coal-based fuel, which also had a RCO to LCO ratio of 1:1 (designated X-610), are also included.

The results clearly show that the sooting propensity characteristics for JP-900 are comparable to those of JP-8. Additionally, they illustrate the remarkable improvement in sooting characteristics of the prototype JP-900 as compared to earlier coal-based fuels. Combined with previous results for the combustion instability and CO and NOx emissions for JP-900, which indicated again quite similar behavior as observed for JP-8, the potential use of this coal-based JP-900 as a replacement for JP-8 in heat-load aviation environments where thermal stability is critical is very promising.

Combustion Studies of Coal-Based JP-900 at High-Temperature and High-Pressure Conditions

An integrated comprehensive experimental effort that investigated the key processes of injection, atomization, vaporization and mixing for coal-based JP-900 and more conventional

fuels was studied. The experiments were geared towards characterizing the fundamental injection behavior of JP-900 and simpler hydrocarbon fuels and simulants over the range of conditions including sub- to super-critical fuel pressures and temperatures.

These studies investigated injection of two coal-based RCO/LCO blends (1:1 (X610) and 3:1 (X620)) of prototype JP-900, as well as JP-8 into a combustion chamber at approximately 6.9 MPa (1000 psia), a supercritical pressure for all fuels considered. The RCO/LCO terminology refers to the ratio of refined chemical oil (RCO), a coal-based component, to light cycle oil (LCO), a petroleum-based component, in the fuel. Both the X610 and X620 were hydrotreated (HDT) which reduces heteroatoms such as nitrogen and sulfur while adding to the hydroaromaticity of the fuel. The fuels are pre-heated and injected at sub- or super-critical temperature into a subsonic (~2-3 m/s) cross-flow which has a temperature of about 922 K (1200°F). The critical properties of JP-8 are approximately 673 K (750°F) and 2.2 to 2.3 MPa (320-485 psia), depending on the formulation. The critical properties of 1:1 RCO/LCO (X610) are estimated to be T_c=739 K (870°F) and P_c=3.65 MPa (529 psia). Shadowgraph imaging was employed to visualize the injection process using a CCD camera synchronized with a strobe flash of approximately 3 μs duration.

Figures 8 and 9 include example images for JP-8, and 1:1 RCO/LCO (X610) injection covering the range of injection conditions. Images shown in these two figures for JP-8 and prototype JP-900 fuel (X610) respectively are for transcritical injection conditions. Note that transcritical injection refers to the injection of a fluid at supercritical pressure but subcritical temperature into an environment that is at a supercritical temperature in reference to the injectant. In all cases in this study, the fuel was heated, but to a lesser degree for the transcritical injection cases such that the injection temperature was below the critical value. With the

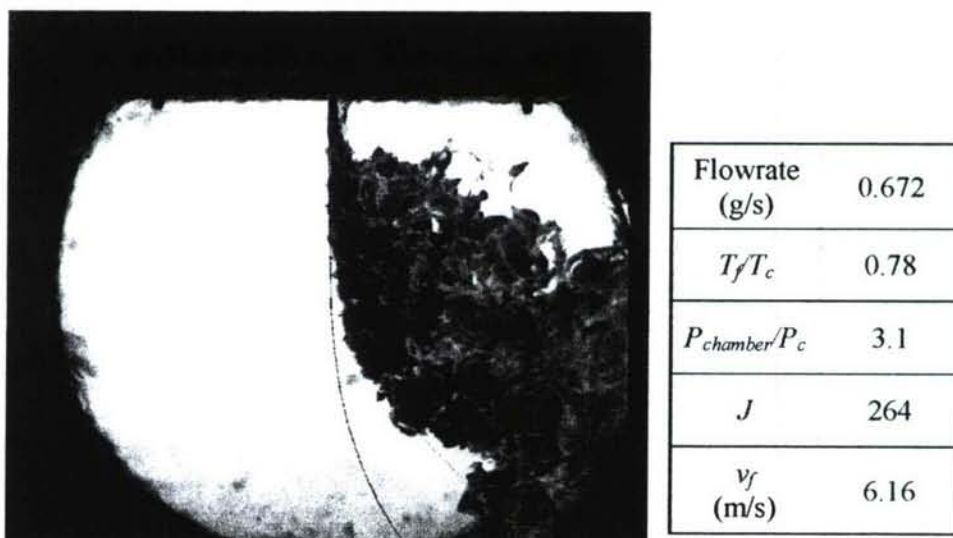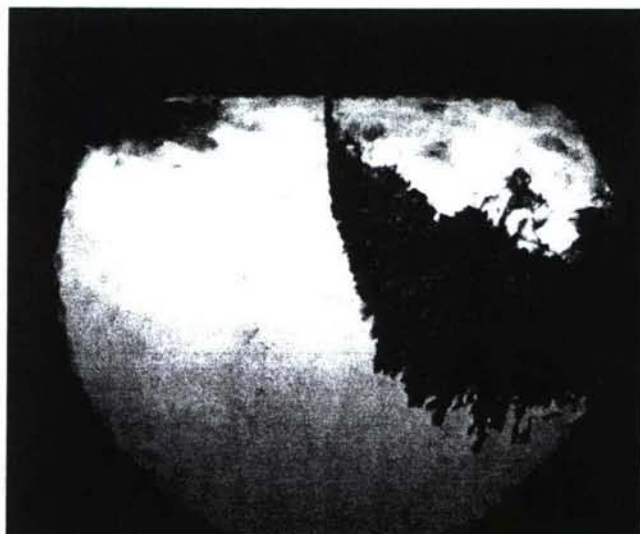| Flowrate (g/s)	0.672
T_f/T_c	0.78
$P_{chamber}/P_c$	3.1
J	264
v_f (m/s)	6.16

Figure 8. Image of transcritical JP-8 injection. Red curve is Lin et al.'s correlation for a subcritical liquid injected into a cross-flow, $y/d=2.42J^{0.48}(x/d)^{0.24}$. Green curve represents new Penn State correlation based on data from this study for a trans- and super-critical fuel injected into a cross-flow, $y/d=2.94J^{0.35}(x/d)^{0.33}$.

Flowrate (g/s)	0.672
T_f/T_c (estimated)	0.88
$P_{chamber}/P_c$ (estimated)	1.9
J	N/A
v_f (m/s)	N/A

Figure 9. Example image of transcritical 1:1 RCO/LCO (X610) injection. Correlation curves are not included because a suitable equation of state to calculate the density at elevated temperature and pressure is not yet available for this mixture or X620.

example images, a few injection quantities are included: mass flowrate, reduced temperature of the fuel measured just prior to injection (T_f/T_c), reduced pressure of the fuel at the injector exit ($P_{chamber}/P_c$), momentum flux ratio of fuel jet to the cross-flow ($J=\rho_f v_f^2/\rho U^2$, where ρ_f is the fuel density in the injector, v_f is the fuel jet average cross-sectional velocity at the injector exit, and ρU^2 is the momentum flux of the cross-flow), and fuel jet average cross-sectional velocity at the injector exit (v_f).

Figure 8 also includes red and green lines overlaid on the images; these curves represent jet penetration correlations corresponding to the injection conditions. The red curves result from the application of a jet penetration correlation determined by Lin et al. for a pure liquid in subsonic cross-flow. This correlation obtained from subcritical fuel injection measurements is based on the momentum flux ratio, J, of the fuel jet to the cross-flow and has the form: $y/d=2.42J^{0.48}(x/d)^{0.24}$, where y is the penetration height, d is the injector diameter, and x is the axial distance downstream of the injector. This correlation, although obtained for subcritical injection conditions, provides a reasonable fit to the jet leading-edge penetration profile for trans- and super-critical injection conditions for both n-heptane and JP-8. A new correlation of the same form as that of Lin et al. was generated using the image data of trans- and super-critical fuel injection from the jet fuel combustion experiments of this report. This new jet penetration correlation has the form: $y/d=2.94J^{0.35}(x/d)^{0.33}$. This correlation was used to generate the green curves shown in Fig. 8. Note that Fig. 9 does not have the correlation curves added or any injection parameters listed related to density because an equation of state for the RCO/LCO blended fuels is yet lacking. Without the fuel density as a function of pressure and temperature, the jet penetration cannot be predicted from the correlations for these cases. Also, note that the density of JP-8 was calculated for the injection conditions using a surrogate mixture of compounds as described in Edwards and Maurice.
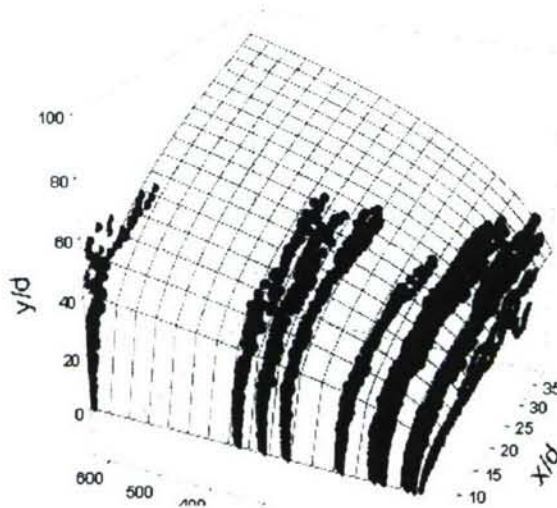
Figure 10. The Penn State correlation for penetration of trans- and super-critical fuel (*n*-heptane and JP-8) jets in a low-speed cross-flow is represented by the surface in this 3-D plot. ($y/d=2.94J^{0.35}(x/d)^{0.33}$) Data points correspond to measured jet penetration profiles from several images.

The new correlation for penetration of trans- and super-critical fuel (n-heptane and JP-8) jets in a low-speed cross-flow is represented by the surface in the 3-D plot of Fig. 10. The jet penetration profiles used to generate the correlation are evident. These profiles were manually extracted from images processed with standard edge-detection algorithms. As evident in Fig. 10, the correlation was based on data covering an order of magnitude in momentum flux ratio, $\sim$60$\leq$J$\leq\sim$600. The coefficient of determination, R^2, for the correlation is 0.966.

Combustion Tests in T-63 Turboshaft Engine

A preliminary evaluation of the characteristics of JP-900 was performed using a T63-A-700 turboshaft engine at the Air Force Research Laboratory. A specification for JP-8 (POSF 3773) was also tested to provide a comparison for the particulate and gaseous emissions produced by the coal-based fuel. The engine was operated at two power settings, designated as ground idle and normal rated power (also referred to as cruise). The fuel flow rate was adjusted during testing to maintain a constant turbine outlet temperature (e.g., power output) for a given setting. This assured the best run-to-run reproducibility and provided a constant basis of comparison for JP-900 and JP-8. The engine was initially operated using baseline JP-8. Operation was then transitioned to the coal-based fuel. Upon completion of the evaluation of JP-900, operation was transitioned back to baseline JP-8 to verify that the emissions returned to the initial (baseline) levels.

JP-900 produced slightly higher particulate and gaseous emissions at the lower power condition with less difference at the cruise condition. The particle number density (PND) emissions for the coal-based fuel were approximately 14.4% and 3.5% higher than those for JP-8

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Table 4. Comparison of smoke number and mass concentration emissions for JP-900 and JP-8 during testing on a T63 turboshaft engine at idle and cruise power conditions.

Engine Condition	Fuel	Smoke Number		Quartz Filter		TEOM	
		Smoke Number	% Increase	Mass Conc. (mg/m^3)	% Increase	Mass Conc. (mg/m^3)	% Increase
Idle	JP-8 (3773)	7.3	23.4	5.7	41.5	3.0	9.5
	Coal-Based	9.6		8.0		3.3	
Cruise	JP-8 (3773)	37.0	9.5	9.2	16.7	10.5	8.5
	Coal-Based	40.7		10.8		11.4	

(POSF 3773) at the idle and cruise conditions, respectively. A comparison of the mass concentration and smoke number emissions is shown in Table 4 [Balster et al., 2007]. These measurements showed an increase in the particulate matter production for JP-900. The smoke number and carbon mass quantified via TPO showed a substantial increase at the idle condition. The qualitative volatile and elemental carbon fractions of the particulate were similar for JP-900 and JP-8, supporting the assertion that the soot formation mechanisms are similar. Increases in carbon monoxide of approximately 21% at idle and 18% at cruise were observed with JP-900. The total unburned hydrocarbons also increased with the coal-based fuel by approximately 30% at idle with negligible differences at cruise. The increased CO and soot production indicated that the overall combustion efficiency of the coal-based fuel was lower than that for the JP-8. There was a mass fuel consumption penalty also observed for the coal-based JP-900 during testing. Although the volumetric fuel flow rate to the combustor was lower for the coal-based fuel (4.8%-idle and 3.3%-cruise) during testing, when accounting for the density difference of the fuels (0.80 g/cm^3 versus 0.87 g/cm^3) there was an increase of approximately 3.5% and 5.1% in the required mass flow rates for the coal-based fuel to maintain the identical power output.

Although JP-900 showed emission increases relative to JP-8, the magnitude of the changes were significantly lower than those observed during a previous study investigating the effect of fuel chemical composition on the emissions [Corporan et al., 2004]. The increases observed in the PND emissions with a fuel high in aromatics (~41%) and cycloalkanes (designated JP-8X 45) and the decreases for one comprised primarily of normal alkanes (Norpar-13) during the previous study are compared to those for JP-900 in Table 5. The magnitude of the differences for the coal-based fuel is much lower than for the previously tested fuels. Comparison of the results from JP-900 testing implies that the overall emissions produced are most likely similar or only slightly greater than those for a typical JP-8. It should be noted that

Table 5. Comparison of percentage change in particle number density emissions relative to JP-8 for JP-900 and Norpar-13 on a T63 turboshaft engine at idle and cruise power conditions.

Engine Condition	Coal-Based Fuel	NORPAR-13	JP-8X 45
Idle	14.4%	-97%	362%
Cruise	3.5%	-62%	854%

the current study did not account for chemical changes that the fuel will undergo if thermally stressed under high-heat sink applications (e.g., formation of unsaturated and aromatic compounds). Since a higher aromatic content increases combustor particulate matter emissions, subsequent emission studies of the coal-based fuel following thermal stressing are warranted if its ultimate use is for applications where significant alterations to the chemical structure are expected.

Pulse Detonation Engines

Pulse detonation engines (PDE) provide the potential for higher specific impulse, reduced complexity and lower operational costs as compared to current gas turbine technology. PDEs represent a revolutionary approach to propulsion and one that can benefit significantly from fuels development such as involved in the JP-900 research program. The coal-based fuels may have compositional and density characteristics that are advantageous for PDEs. Because PDEs are a relativity new engine concept, much of the work undertaken focused on basic phenomena important in establishing the initiation and propagation of detonations under PDE operational conditions. Thus, stimulant fuels, particularly ethene and propane, were used.

A series of studies was conducted to explore the use of the increase in strength of the overdriven detonation as a means to reduce the diffraction effect caused by the area expansion and to initiate a thrust tube detonation. The results indicated that the localized explosion must be positioned within a range of distances near the area expansion in order to utilize the increase in strength of the overdriven detonation. An excessive distance between the last obstacle and the transition section would allow the overdriven detonation to decay back to a detonation wave that would fail to transition into the thrust tube. Similarly, if the distance between the last obstacle and the transition section were too small, the accelerating deflagration wave would be slowed by the increase in cross sectional area before a localized explosion could occur and only a deflagration would exit the thrust tube. Also, generating an overdriven detonation wave in the pre-detonator is a key parameter for obtaining a thrust tube detonation transition.

The diffraction of Chapman-Jouget (C-J) and overdriven detonation waves through a gradual area expansion was investigated using soot foil records of the area expansion and main chamber, simultaneous shadowgraph and CH* chemiluminescence images, and CH* chemiluminescence images taken with long exposure times. The results demonstrate a substantial loss of strength and transverse wave structure of the C-J detonation beyond the wedge of influence, which results in a failure to initiate a thrust tube detonation. Positioning the overdriven detonation in the vicinity of the area expansion entrance can substantially reduce detonation diffraction within the area expansion such that a direct main chamber detonation is initiated. The effect of the overdrive is an increase in the number of detonation cells in the pre-detonator such that the chance of transverse waves surviving the expansion process is greatly increased. Transverse detonations are generated as a result of reflections of these waves off the transition section walls. Additional interaction of transverse detonations with non-reactive transverse waves generates locally overdriven detonations which reignite the detonation. This process is seen to occur either within the transition section or in the main chamber immediately downstream from the exit of the transition section.

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PERSONNEL

Faculty

Andre Boehman, Michael Coleman, Semih Eser, Daniel Haworth, Peter Luckie, Michael Micci, Robert Santoro, Harold Schobert, Chunshan Song, Robert Waston, Vigor Yang

Research Staff and Postdoctoral Researchers

Parvana Aksoy, Orhan Altin, John Andresen, Mark Badger, Jean-christophe Broda, Christophe Brossard, Caroline Burgess Clifford, David Clifford, Josefa Griffith, Omer Gul, Maria Klimkiewicz, John Larsen, Seong-young Lee, Xiaoliang Ma, Jonathan Mathews, Gary Mitchell, Anne Mouis, Richard Neumann, Sibtosh Pal, Andrzej Piotrowski, Silvano Saretto, Maria Sobkowiak, Srimat Srinivas, Richard Steinberger, Roger Woodward

Support Staff

Carol Brantner, Teresa Carmody, Ronald Copenhaver, Jaime Crissinger, Donna Dean, Glenn Decker, Kurtis Decker, Howard Glunt, Amanda Herriman, Larry Horner, David Johnson, Bradley Maben, Bradley Moulton, Ronald Nargi, Mary Newby, John Raiser, Shannon Ranio, Kelly Rhoades, Larry Schaaf, Abby Smith, Virginia Smith, Ronald Wasco, Ronald Wincek, Kevin Witt, Elizabeth Young, James Zello

Graduate Research Assistants

Ryuichi Ashida, Scott Berkhous, Elise Bickford, Nicolas Bouvet, Abraham Brandt, Justin Brumberg, Suchada Butnark, Elana Chapman, Silvio Chianese, Jennifer Clemons, Christopher Conrad, John Cramer, Dustin Davis, Vasudha Dhar, Richard Dutta, Maria Escallon, Kathryn Fisher, Patrick Flynn, Aric Glass, Christopher Greene, Mayumi Greene, Weidong Gu, Kevin Guigley, Peter Hammond, Howard Hess, Shih-yang Hsieh, Ying Huang, Gregory Jensen, Deepa Kannan, Sanjeev Khanna, Steven Kirby, Elena Korobetskaya, Kyle Landry, Matthew Lehman, Yan Li, Kurt Ludwig, William Marshall, Matt Mckeand, Travis Mells, Arvind Menon, Ashok Mishra, Christopher Mordaunt, Peter Pappano, Bryan Quay, Arun Ram Mohan, Melissa Roan, Brian Senger, Jingyan Shao, Rafat Shehadeh, Jian-ping Shen, Timothy Spegar, Michael Sprague, James Strohm, Uday Turaga, Ramya Venkataraman, Jonathan Watts, Yuhui Wu, Rongjie Yang, Minggang Yang, Yi Yang, Danning You, Jian Yu, John Zengel, Jian Zheng, Nan Zong

Part-time Employees (Including Undergraduate Students)

Jean-philippe Alphonse Kouassi, Oyku Asikoglu, Geoffrey Bock, Jeff Borck, Michael Boyer, Timothy Brett, Todd Brieck, Ben Carlsen, Jean-marc Celsa, Jennifer Delecce, Sarah Edwards, Anne Fickinger, Kathryn Fisher, Julien Fort, Melanie Fox, Christina Gallo, Jessica Goodeluinas, William Greenland, Elizabeth Grobe, Dionne Hallett, Nate Herman, Sara Hillegas, Matthew Hoehn, Mark Jesudowich, Brice Junsop, Kevin Kelleher, Dylan Kershner, Terry Keyser, Aparna Krishnamurthy, Rohan Kumar, Fuhua Ma, Manju Mathew, Marcia Mcmillian, David Morris, Sameet Nabar, John Pedlow, Temitope Phillips, Matthew Sebastain, Amy Scalise, Steve Smith, Narashmhan Soundarrajan, Katherine Strass, Lu Sun, Danielle Target, Pailin Vongseng

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INVENTIONS

None.

SIGNIFICANT INTERACTIONS

Political

Throughout the life of this project there were numerous interactions with, and briefings for, interested members of the Pennsylvania congressional delegation, specifically former senator Rick Santorum and congressmen John Murtha and John Peterson. These always involved one or more persons from the member's staff, and often face-to-face meetings with the member himself. Typically these meetings were on an ad hoc basis, but occurred at least annually.

Other Governmental Agencies

Beginning in September 2005, there have been a series of informational exchanges with the Appalachian Regional Commission, primarily with Mr. Rick Peltz. In principle, ARC might be interested in providing modest assistance for commercialization of the coal-to-liquids processes developed as part of this project.

A briefing was provided for staff of the Federal Aviation Administration in summer 2006.

Air Force

Briefing and laboratory tour was provided for former Deputy Assistant Secretary James Engle in December, 2004.

Private Sector

Throughout the duration of this project, there have been numerous discussions with many companies and investors in an effort to attract sufficient private-sector interest to commercialize production of JP-900 and its ancillary products. The largest of the companies briefed included American Airlines (March 2006), Chevron (October 2006), and Sasol (November 2006). The other end of the spectrum includes such small business operations as Innodyn (manufacturer of gas turbine engines, June 2006), Liquid Coal (a coal-to-liquids company, January 2006), and RC Energy (a coal producer, August 2006).

The most important of these interactions was the so-called Jet Fuel Summit meeting, held at Penn State in June 2006. Among the companies and agencies represented at this meeting were Air Force Research Laboratory, American Airlines, Appalachian Regional Commission,

Chevron, Congressman Peterson's Office, Conoco Phillips, Duquesne University, Energy Technology Consultant, Federal Agency Liaison Office, Federal Aviation Administration, HQ Air Combat Command, Intertek(PARC), Koppers Industries, MountainTop Technology, NASA, Pratt & Whitney, Saminco Electric Traction Drives, Schobert International, Sorensenergy, LLC., Southwest Research Institute, The Pennsylvania State University, Wright-Patterson Air Force Base.

Partly as a result of this summit meeting, a start-up company, at least one start-up company has been formed for the purpose of commercializing the coal-to-liquid technology developed here. Strictly speaking, most of these activities fall after the reporting period covered in the present report. Hopefully it will be possible to provide much more information, if these efforts come to fruition, in succeeding reports.

ABBREVIATIONS AND ACRONYMS

AFOSR	Air Force Office of Scientific Research
ASTM	American Society for Testing and Materials
C	Celsius
C-J	Chapman-Jouget
cm	centimeter
DOD	Department of Defense
EAS	electrophilic aromatic substitution
ECAT	equilibrium catalyst
F	Fahrenheit
FT	Fischer-Tropsch
g	gram
i.d.	inside diameter
K	kelvins
LCO	light cycle oil
MPa	megapascal
min	minute
mL	milliliter
o.d.	outside diameter
PDE	pulse detonation engine
PND	particle number density
POSF	Ports of Support File
psig	pounds per square inch, gauge
QCM	quartz crystal microbalance
RCO	refined chemical oil
s	second
µg	microgram